Plating & Surface Finishing Retrospective

Originally contributed by Ronald Kornosky Compiled by Dr. James H. Lindsay, AESF Fellow

Based on an original article from the early "Finishers Think Tank" series [Plating & Surface Finishing, **69**, 19 (February 1982) and **69**, 20 (March 1982)]

Sulfate in rhodium bath

Q: Is there a simple way to determine the sulfate content in a rhodium plating solution?

A: There are several ways, but the most simple I know of is as follows:

- 1. Pipet 10 mL of solution into a 250-mL Erlenmeyer flask.
- 2. Add 100 mL of deionized water and two drops of 0.2% methyl orange solution.
- 3. Titrate with 1.0N sodium hydroxide (NaOH) until the color changes (pink at pH 3.2 to yellow at pH 4.4) or use a pH meter to check.
- 4. To calculate the cc/L of sulfuric acid, multiply the milliliters of sodium hydroxide used times 2.8.

Other methods such as (1) total sulfate by gravimetric determination and (2) a rapid modification of the gravimetric method - along with their theory and limitations - are discussed by K. Langford and J. Parker in *Analysis of Electroplating and Related Solutions*, available through the AESF or directly from Portcullis Press Ltd., Queensway House, 2 Queensway, Redhill, Surrey RH1 12S, England.

Barrel zinc problem

Q: Our zinc barrel plating line for steel parts has been giving us thickness problems. We plate a load size of 75 ft^2 for 40 min at 425 A to achieve a thickness of 0.0003 \pm 0.0001 in. Our thickness-measuring device, however, shows that the deposit on one side of the part exceeds this thickness spec and that the plate on another area is consistently thinner. Because the parts are being tumbled in a barrel, we feel a more uniform deposit should be the result. What do you think?

A: A quick check of your figures shows that the calculated zinc deposited at even 100% efficiency would be an average of only 0.00026 in (6.6 μ m) in thickness. Also, keep in mind that any bright dip after plating could remove some zinc, depending on time of immersion, temperature and

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concentration of the solution. A longer plating time should give you the required thickness.

Uniformity is not always assured in a barrel containing flat parts. I noted that the side of the part with the thickest plate has a tab bent at about a 15° angle, which may be separating it from the remainder of the plating batch, providing sufficient solution and current flow. Try mixing other easily separable parts with your regular batch or modify the speed of your barrel rotation.

Plating non-conductors

Q: I'd like to plate real leaves, seed pods and selected flowers. Any help you can offer will be appreciated.

A: The key to plating non-conductive surfaces is proper preparation. In this case, many thin coats of a spray lacquer should be used to build up a hard surface that is not porous and that cannot absorb any moisture. After this is done, there are several things that can be used, including a spray of fine copper powder mixed with lacquer thinner, or conductive paint with nitrocellulose lacquer and copper powder. The material, when sprayed, should be dull, showing that the copper - and not the lacquer - is predominant on the surface.

A mirroring process, in which silver or copper, for example, is mixed with a reducing agent to chemically precipitate the metal on the surface, also is useful. After these steps, the item can be plated like any other conductive material. More information can be found in *Electroplating and Electroforming for Artists and Craftsmen*, by Lee Scott Newman and Jay Newman, Crown Publishers, Inc., One Park Ave., New York, NY.

Brass on castings

Q: We have been trying unsuccessfully to plate white metal castings, for example, 2.0% tin, 8.0% antimony and 90% lead; or 24% tin, 2.0% antimony and 74% lead. After plating with cyanide copper for 15 to 20 min, with Watts nickel for 20 to 30 min and with brass for 30 to 45 min, we send the parts back through the cleaning cycle. The brass then is blackened, dried and relieved. The parts, however, normally start to spot-out within 30 min.

A: Bleedout of brass has been a problem as long as brass plating itself has existed. The obvious solutions – rinsing with alternating hot and cold water, dipping in mild acids and ultrasonic cleaning – you have tried. Pores in the surface of the casting retain corrosive chemicals that react with the deposit.

A soak in 3.0% bleach (sodium hypochlorite) solution may help. Proper passivation of the brass after blackening also may be useful. Your supplier has a brass passivating salt to prepare a dip or even an electrolytic alkaline chromium-containing type that evolves hydrogen gas to scrub the parts.

Because voids are the problem, perhaps a bright leveling nickel or acid copper as a replacement for the Watts nickel would constitute an improvement.

Hard chromium solutions

Q: We are plating hard chromium on cylinders and would like any information you can provide on all-sulfate baths versus the mixed-catalyst types.

A: During chromium plating, the ratio of chromic acid and catalyst should be controlled carefully to get the best possible covering power and efficiency. Besides sulfate, another catalyst that is sometimes used is fluosilicate. Self-regulating versions of these baths employ a slightly soluble fluosilicate compound and a slightly soluble sulfate compound (*e.g.*, strontium sulfate). The solubility of both varies with temperature, of course.

A comparison of cathode current efficiency for similar baths with a specific gravity of 1.179 at 110°F (43°C) is given in Table 1. The comparative plating speeds under the same conditions are shown in Table 2. At low current densities, the mixed-catalyst bath is the best.

Table 1 – Comparison of hard chromium baths.									
Current density		Cathode efficiency, %							
A/ft ²	A/dm ²	Mixed bath	All-sulfate						
36	3.9	8.1	4.9						
72	7.8	12.5	9.6						
144	15.5	17.0	14.9						
288	31.1	23.0	18.5						

Table 2 – Plating speeds of hard chromium baths									
	Plating rate								
Current density		Mixed bath		All-sulfate					
A/ft ²	A/dm ²	mil/hr	μ m/hr	mil/hr	μ m/hr				
72	7.8	0.18	4.57	0.14	3.55				
144	15.5	0.48	12.19	0.43	10.92				
288	31.1	1.24	31.49	1.06	26.92				

Thickness measuring

Q: We deposit electroless nickel on ceramic tubes during 7 min in a 160° F (71°C) bath. Then, we electroplate tin with a stannous sulfate acid bath. What method, other than recording the length of time in each bath, can we use to determine the thickness of each plate?

A: You must take several things into consideration, including the thickness of the deposit, the complexity of the part and the expected reliability, when selecting a thickness-measuring technique. The microscopic method is time-consuming and requires a high degree of skill for thin deposits such as that produced during 7 min of plat-

ing nickel-phosphorus alloy. Any other method should give you good results on tin, but the electroless nickel, being a phosphorus alloy, may present a problem. Coulometric methods developed for nickel and tin may be applicable if your electroless deposit has a thickness of at least 5 μ -in. (0.125 μ m), but, if a non-destructive method is desired, other techniques such as beta backscatter should be considered. Vendors of thickness-measuring instruments should be consulted for specific recommendations.

Dissolved anode basket

Q: Our titanium anode baskets dissolved (Fig. 1) in an acid zinc bath. The voltage on the barrel line is 10 to 11V. After two months of operation, the problem arose. What should we do?



Fig. 1-Titanium anode baskets dissolved in zinc bath.

A: Titanium usually forms an oxide film, preventing it from corroding in many plating baths. The bipolar nature of this film permits current flow into another metal in contact with it, but not into the solution. Any voltages above 8 or 9 will cause an attack of the film, resulting in the problem you describe. Rather than reducing the voltage and thereby sacrificing amperes per square foot, try using cast or slab zinc anodes and titanium hooks. And remember to keep the top of the anode - where the hook is attached - above the solution level.

Best pH for effluent

Q: The effluent from our waste-treatment system varies in terms of heavy-metal concentrations. We plate copper, nickel and chromium on zinc die castings. What would be the best pH for the final effluent?

A: Without a study of the housekeeping practices and plumbing in your shop, I can only assume that segregation of waters containing cyanide, chromium and other materials has been performed. With the cyanide properly destroyed, and the chromium satisfactorily reduced to the trivalent state, the resulting mixture will be pH adjusted. A textbook shows that the minimum solubility of these hydroxides, formed with sodium hydroxide, is as indicated in Table 3.

As shown, the highest pH favors the best precipitation, in most cases. A pH of about 9.5 should be best. One thing that may keep you from reaching these low numbers is the wetting / complexing agent in your cleaners. They react with the metals and tie them up to varying degrees. Good housekeeping -i.e., removing parts that

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Table 3 – Minimum solubility figures, mg/L								
Metal	р Н 8.0	рН 8.5	рН 9.0	рН 9.5	рН 10.0			
Copper	0.0050	0.0002	0.0001	0.0003	0.0010			
Nickel	6.0	0.7	0.1	0.007	0.001			
Chromium	0.03	0.02	0.03	0.10	0.50			
Zinc	8.0	0.20	0.07	0.10	0.30			

have fallen into tanks – should help keep the zinc out. These metal hydroxides are hard to settle. But the use of lime, instead of caustic, for precipitation results in a precipitate with much better settling properties, but at a higher cost with a greater volume of sludge.

Proper use of polyelectrolytes, especially mixtures of two or more types, should aid settling in shorter periods of time. The type of equipment and the time allowed for settling also are important factors. A lot of sample testing and lab work will payoff by checking all of these parameters.

Blackening problem

Q: We plate brass and bronze on steel and zinc die castings, and then blacken with a liquid polysulfide. The problem we have is color matching and getting different shades of black. Is there a better process for our purposes?

A: Oxidizing with polysulfide is the time-honored way of blackening copper or any copper-containing alloy. It is important to have a clean brass surface – one that is not stained or protected by a passive surface. The concentration of polysulfide and the temperature of the bath should be kept constant so that the black color takes about 1 min to form.

Another approach would be to form black nickel - either nickelzinc alloy or nickel-tin alloy -over the clean surface. This would give reproducible results over all alloys. These processes, plus other dips, are available through several suppliers.

Stripper creates pits

Q: I have been using a commercial formulation mixed with sodium cyanide to strip copper and nickel from steel. After awhile, the steel begins to pit, and we change the stripper. What is the alternative?

A: The alkaline nitrobenzene / sulfonic acid sodium salt strippers work very well as long as the cyanide concentration remains high. Therefore, cyanide analysis should be conducted daily to keep the bath within the supplier's specifications. If the cyanide concentration is low, the stripper will pit the steel. Also, the higher the temperature of the bath, the shorter will be the life of the stripper.

Anodizing spots

Q: What's causing the white spots to form on the black anodized parts enclosed? Most of the parts lately seem to be cursed with these spots.

A: Examination of the components indicates that the parts are very porous. It appears your sulfuric acid anodizing solution was not properly rinsed from the parts and that, at some time after processing, it dissolved the dye, leaving the spots. Alternating hot and cold rinses may help, along with ultrasonic agitation. The final solution, however, rests with the company manufacturing the castings. If they will provide a less-porous material, your problem will disappear. *P&SF*

Editor's note: The edited preceding article is based on material compiled by Mr. Ronald Kornosky, then of Hager Hinge Co., in Montgomery, AL, as part of the Finishers Think Tank series, which began its long run in this journal 26 years ago. It dealt with everyday production plating problems, many of which are still encountered in the opening years of the 21st century. As we have often said, much has changed ... but not that much. The reader may benefit both from the information here and the historical perspective as well. For many, it is fascinating to see the analysis required to troubleshoot problems that might be second nature today. In some cases here, words were altered for context.



Theory and Practice of Pulse Plating

Edited by Dr. Jean-Claude Puippe and Frank Leaman

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Pulse plating offers exciting alternatives for surface finishers, and *Theory and Practice* of *Pulse Plating* provides up-to-date information on this relatively uncharted territory. Dr. Jean-Claude Puippe and Frank Leaman have assembled an international forum of authors to present detailed discussions on every aspect of pulsed electrodeposition of zinc and cadmium, nickel and chromium, precious metals, ruthenium, and alloys. A separate chapter covers pulsed anodic reactions.

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